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Effect of industrial pollution on the behaviour of $^{239,240}\text{Pu}$, ^{241}Am and ^{137}Cs in forest ecosystems

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Academic Dissertation

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ABSTRACT

The behaviour of radionuclides ($^{239,240}\text{Pu}$, ^{241}Am and ^{137}Cs) was investigated in forests in the vicinity of Cu-Ni smelters in Monchegorsk, Russia, and Harjavalta, Finland. Study was made of the effect of industrial pollution on the distribution of radionuclides between various soil horizons, on their chemical forms in the organic horizon and on soil-to-plant transfer. Sampling sites in Monchegorsk were in spruce forest, while those in Harjavalta were in pine forest.

Industrial pollution had a significant effect on the behaviour of radionuclides in forest ecosystems. As the load of industrial pollution increased towards the smelter, more radionuclides accumulated in the litter layer and less in the organic horizon. This trend was due to the inhibited microbial activity in the vicinity of the smelters, which caused slower decomposition of litter into organic matter. Pollution also affected the chemical forms of radionuclides, and less 'easily exchangeable' (plant available) radionuclides were present in the organic layer at the most polluted sites.

The effect of industrial pollution on the transfer of radionuclides from soil to plant depended on the radionuclide, plant species and forest type. In pine forest, soil-to-plant transfer of ^{137}Cs was noticeably reduced in the vicinity of the smelter, while transfer of $^{239,240}\text{Pu}$ and ^{241}Am from soil to plants was less affected. In spruce forest, soil-to-plant transfer of $^{239,240}\text{Pu}$ increased for most species with increasing industrial pollution owing to surficial contamination of plants by resuspended soil. Soil-to-plant transfer of ^{241}Am was generally higher than that of $^{239,240}\text{Pu}$.

PREFACE

The work for this thesis was carried out in the Laboratory of Radiochemistry, University of Helsinki, during the years 1997- 2002.

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LIST OF PUBLICATIONS

The thesis is based on the following papers, which are referred to in the text by their Roman numerals. Note name change from Riekkinen to Outola.

- I Puhakainen M, Riekkinen I, Heikkinen T, Jaakkola T, Steinnes E, Rissanen K, Suomela M, Thørring H. Effect of chemical pollution on forms of ^{137}Cs , ^{90}Sr and $^{239,240}\text{Pu}$ in Arctic soil studied by sequential extraction. *J Environ Radioactivity* 2000; 52(1): 17-29.
- II Bunzl K, Puhakainen M, Riekkinen I, Karhu P, Schimmack W, Heikkinen T, Jaakkola T, Nikonov V, Pavlov V, Rahola T, Rissanen K, Suomela M, Tillander M, Äyräs M. Fallout ^{137}Cs , ^{90}Sr and $^{239+240}\text{Pu}$ in soils polluted by heavy metals: Vertical distribution, residence half-times, and external gamma-dose rates. *J Radioanal Nucl Chem* 2001; 247: 15-24.
- III Riekkinen I, Jaakkola T. Effect of industrial pollution on soil-to-plant transfer of plutonium in a Boreal forest. *Sci Total Environ* 2001; 278: 161-170.
- IV Outola I, Pehrman R, Jaakkola T. Effect of industrial pollution on distribution of ^{137}Cs in soil and its soil-to-plant transfer in a pine forest in SW Finland. *Sci Total Environ*, in press.
- V Outola, I. Effect of industrial pollution on distribution of Pu and Am between various soil horizons and on soil-to-plant transfer of Pu and Am in a pine forest in SW Finland. Submitted for publication in *J Radioanal Nucl Chem*.

CONTENTS

ABSTRACT	1
PREFACE	2
LIST OF PUBLICATIONS	3
1. INTRODUCTION	5
2. BEHAVIOUR OF RADIONUCLIDES ($^{239,240}\text{Pu}$, ^{241}Am, ^{137}Cs) IN FOREST ECOSYSTEMS	7
2.1 Forest ecosystems	7
2.2 Environmental sources of plutonium, americium and radiocaesium, and their oxidation states in the environment	8
2.2.1 Environmental sources	8
2.2.2 Oxidation states	9
2.3 Speciation of radionuclides in soil studied by sequential extraction	9
2.4. Behaviour of radionuclides in soil	10
2.4.1 Pu and Am in soil	10
2.4.2 Radiocaesium in soil	12
2.5 Soil-to-plant transfer of radionuclides	14
2.5.1 Soil-to-plant transfer of Pu and Am	14
2.5.2 Soil-to-plant transfer of radiocaesium	15
3. SAMPLING SITES AND METHODS	18
3.1 Sampling sites	18
3.2 Sampling	22
3.3 Analytical methods	23
4. RESULTS AND DISCUSSION	25
4.1 Radionuclides in forest soils contaminated by industrial pollution	25
4.1.1 Distributions of $^{239,240}\text{Pu}$ and ^{241}Am in soil	25
4.1.2 Distribution of ^{137}Cs in soil	27
4.1.3 Total deposition of radionuclides in soil	28
4.2 Effect of industrial pollution on chemical forms of radionuclides in forest soil	29
4.2.1 Chemical forms of $^{239,240}\text{Pu}$ and ^{241}Am	29
4.2.2 Chemical forms of ^{137}Cs	30
4.3 Effect of industrial pollution on radionuclides in vegetation	31
4.3.1 $^{239,240}\text{Pu}$ and ^{241}Am in vegetation	32
4.3.2 ^{137}Cs in vegetation	32
4.4 Effect of industrial pollution on soil-to-plant transfer of radionuclides	33
4.4.1 Soil-to-plant transfer of $^{239,240}\text{Pu}$ and ^{241}Am	33
4.4.2 Soil-to-plant transfer of ^{137}Cs	35
5. CONCLUSIONS	37
6. REFERENCES	39

1. INTRODUCTION

Widespread radioactive environmental pollution has resulted from the atmospheric nuclear weapons testing carried out during the 50's and 60's. Other radioactive releases to the environment have been associated with nuclear fuel cycles and various accidents. The Chernobyl accident in 1986 renewed interest in the behaviour of radionuclides in the environment. Radiation doses of humans are received through exposure to radionuclides on the ground, by internal ingestion or by inhalation. The long-term behaviour of radionuclides in the environment thus needs to be understood in a comprehensive way.

Forests are an important source of radioactivity to humans through the consumption of berries, mushrooms and game. Radionuclides are available for plants in forest ecosystems much longer than they are in agricultural ecosystems (Bürmann et al., 1994). Because of their peculiar climate and soil properties, Boreal forests are especially sensitive to chemical pollutants, which in turn affect the behaviour of radionuclides and of essential nutrients in these ecosystems. In the event of an accident at a nuclear facility where radionuclides were released to the environment, understanding of the effect of industrial pollution on the behaviour of radionuclides, and also on the radiation risk, would be crucial.

The aim of this study was to investigate how and to what extent industrial pollution affects the behaviour of radionuclides in forest ecosystems. Study was made of the effect of industrial pollution on the distribution of radionuclides in soil, on their chemical forms in the soil and on the soil-to-plant transfer. The study was conducted in the vicinity of two Cu-Ni smelters: one in a pine forest at Harjavalta, Finland, and the other in a spruce forest at Monchegorsk, Russia. In Monchegorsk, the radionuclides mainly originated in atmospheric nuclear tests, whereas in Harjavalta, Chernobyl-derived radionuclides were a significant source of Pu and Am and the main source of ^{137}Cs .

Radionuclides selected for study were the long-lived isotopes $^{239,240}\text{Pu}$, ^{241}Am and ^{137}Cs . Transuranium elements in the environment are a concern because of their very long

physical and biological half-lives, their accumulation in bone and liver and their high radiotoxicity values. Americium, which forms by decay of ^{241}Pu , is becoming the major transuranium element in the areas of Chernobyl deposition. ^{241}Am has been studied much less thoroughly than $^{239,240}\text{Pu}$ and more information about the behaviour ^{241}Am , especially in forest ecosystems, is urgently needed. ^{137}Cs was included in the study because the large amount of Chernobyl-derived ^{137}Cs in Harjavalta offered an opportunity to clarify the effects of industrial pollution on its behaviour and thereby better to explain the results obtained for the transuranium elements.

This work included the development of a method for the separation of ^{241}Am from environmental samples. The extraction chromatography used in the procedure allowed faster purification of ^{241}Am than the conventional methods based solely on ion exchange. The extraction chromatography method provided high radiochemical purity.

2. BEHAVIOUR OF RADIONUCLIDES ($^{239,240}\text{Pu}$, ^{241}Am , ^{137}Cs) IN FOREST ECOSYSTEMS

2.1 Forest ecosystems

Forest ecosystems consist of organisms (plants, animals and micro-organisms) and their habitats (soil and air) (Helmisaari, 2000a). In the northern boreal forest the functioning of forest ecosystems is strongly regulated by the severe climate and the relatively nutrient-poor soil (Helmisaari 2000b). As noted by Pennanen et al. (2000), the organic material deposited on and in the soil is decomposed and mineralised primarily through the activity of fungi, bacteria and soil animals, and the nutrients released to the soil are then available for plant uptake. The biological activity of the soil is thus of prime importance in maintaining the fertility of terrestrial habitat.

Natural ecosystems are increasingly subjected to anthropogenic stresses, such as heavy metals, chemical waste, acidification, temperature increase, lowering of the water table and irrigation (Vanderborght, 1990). High concentrations of heavy metals are toxic for soil micro-organisms, and heavy metal accumulation in the soil can affect nutrient cycling throughout the ecosystem by inhibiting litter decomposition (Fritze et al., 1989). Heavy metals may also change the species composition of the cultivatable bacteria and fungi (Fritze et al., 2000). Acidification of the soil changes the structure of the microbial community and lowers the soil respiration rate more on relatively nutrient-poor sites than on fertile sites (Pennanen et al., 2000).

Many heavy metals are essential for plants at low concentrations, but at high concentrations they disturb nutrient uptake and may have direct toxic effects on plant roots and micro-organisms. Mycorrhizas, which provide an interface between roots and soil, are highly effective in assimilating essential metals (Meharg and Cairney, 2000). Mycorrhizal fungi play a key role in the survival of plant species on metal polluted sites: they improve the vitality of the host plant and some of them exhibit a high metal tolerance and are thereby able to protect root growth of their host (Colpaert et al., 2000).

2.2 Environmental sources of plutonium, americium and radiocaesium, and their oxidation states in the environment

2.2.1 Environmental sources

Atmospheric nuclear weapons testing has been by far the greatest source of radionuclides in the environment. About 1.2×10^{16} Bq of $^{239,240}\text{Pu}$ and 2.8×10^{14} Bq of ^{238}Pu have been produced and distributed globally (Hardy et al., 1973). Another major source of plutonium was the accidental burning of satellite SNAP-9A, which released 5×10^{14} Bq of ^{238}Pu (Hardy et al., 1973). The amount of ^{137}Cs produced by nuclear weapons testing is estimated to be 9.5×10^{17} Bq (UNSCEAR, 2000a). The following amounts of activities were released in 1986 as a consequence of the Chernobyl accident: 3.5×10^{13} Bq of ^{238}Pu , 7.2×10^{13} Bq of $^{239,240}\text{Pu}$, 8.5×10^{16} Bq of ^{137}Cs and 5.4×10^{16} Bq of ^{134}Cs (UNSCEAR, 2000b). ^{241}Am has been formed mainly by in situ decay of ^{241}Pu . Atmospheric testing was responsible for release of 1.4×10^{17} Bq of ^{241}Pu and the Chernobyl accident for 6×10^{15} Bq (UNSCEAR, 2000a,b). Other, local sources of these radionuclides include releases from nuclear reprocessing facilities, reactor operation and various accidents. Half-lives of the radioisotopes studied are given in Table 1. Although plutonium is widely regarded as a man made-element, both ^{244}Pu and ^{239}Pu were produced by supernova explosions in the early universe and are in fact natural radionuclides. In addition, there has been continuous low-level production of ^{239}Pu from ^{238}U since the formation of the earth (Taylor, 2001).

Table 1. Half-lives of the radioisotopes studied (Seelmann-Eggebert et al., 1981).

Nuclide	Half-life (years)
^{241}Am	432.6
^{241}Pu	14.4
^{240}Pu	6550
^{239}Pu	24110
^{238}Pu	87.74
^{137}Cs	30.17
^{134}Cs	2.06

2.2.2 Oxidation states

Plutonium can exist in four oxidation states, III, IV, V and VI, in aqueous solutions of the pH and Eh ranges found in nature. The III and IV states may be present as their simple hydrated cations, while V and VI form linear dioxo species Pu(V)O_2^+ and Pu(VI)O_2^{2+} (Choppin, 1988). In general, the oxidation states Pu(IV) and Pu(III) are encountered in solid material and the higher valencies Pu(V) and Pu(VI) predominate in natural waters (Guillaumont and Adloff, 1992). The normal trend in complexation strength is $\text{Pu(IV)} > \text{Pu(VI)} > \text{Pu(III)} > \text{Pu(V)}$ (Choppin, 1988). The redox speciation of plutonium is complicated by such effects as hydrolysis, complexation, disproportionation, solubility, redox interchange reactions and reduction by organic complexants (Choppin et al., 1997). Americium and caesium occur in natural environment predominantly as Am(III) and Cs(I).

2.3 Speciation of radionuclides in soil studied by sequential extraction

Sequential extraction (i.e. the selective dissolution of soil phases with increasingly aggressive chemical treatment) can provide experimental evidence on contaminant partitioning to various soil phases, being useful for predicting the mobility and bioavailability of contaminants in polluted systems (Clark et al., 1996). A major advantage of sequential extraction procedures is that in some degree they simulate the various environmental conditions to which the soil may be subjected (Tessier et al., 1979). All fractions obtained by using selective reagents for the sequential extraction of radionuclides are to some extent only operationally defined. Nevertheless they yield valuable information about relative differences in the association of a radionuclide with soil constituents (Bunzl et al., 1997). Sequential extraction procedures are useful for qualitative interpretation of biological availability but lack sufficient rigour to be useful for quantitative predictions (Hinton et al., 1998).

Sequential extractions typically show that Pu is strongly associated with the organic matter and metal oxides in soil (Bunzl et al., 1995a; Bunzl et al., 1998b; Duff, 2001; Ibrahim and Morris, 1997; Lee and Lee, 2000). Plutonium is largely retained by organic

matter and oxide phases even where very little organic matter is present (Livens and Baxter, 1988). In most soil layers, Am is primarily attached to the soil organic matter but to a considerable extent it is also attached to oxides and minerals (Bunzl et al., 1995a). Relative to Pu, more Am in soil has been found to be in soluble and exchangeable form (Bunzl et al., 1995a; Ibrahim and Salazar, 2000). The content of mobile forms of transuranium elements in soils is relatively low because the transuranic elements form sparingly soluble complexes with high molecular components of soil humus and with Fe, Al and Ca (Sokolik et al., 2001).

Most ^{137}Cs appears to be strongly bound to soil components, especially to mineral matter (Anderson, 1991; Bunzl et al., 1997; Bunzl et al., 1998b; Livens and Baxter, 1988; Riise et al., 1990; Sokolik et al., 2001). The strong fixation of ^{137}Cs in soil has mostly been attributed to its association with interlayer exchange sites in clay minerals (Oughton et al., 1992). Irreversible sorption of ^{137}Cs by soil clay minerals is the reason for the low content of mobile ^{137}Cs forms (Sokolik et al., 2001). On the basis of sequential extraction, Riise et al. (1990) proposed that less than 10% was mobile. In soils with high content of organic matter, the absorption of organic polyanions at the highly selective sites of clay minerals may significantly decrease ^{137}Cs fixation (Sokolik et al., 2001). Speciation studies have shown that radiocaesium is more weakly bound in the lower layers of the soil than in the topsoil (Anderson, 1991; Bunzl et al., 1998b).

2.4 Behaviour of radionuclides in soil

2.4.1 Pu and Am in soil

In several terrestrial ecosystems that have been studied, more than 99 per cent of the plutonium inventory was ultimately associated with soil and less than 1% with biota (Watters et al., 1983). Most of the Pu was accumulated in the upper 10 cm of soils. The location of Pu in soil is important for two exposure pathways: resuspension for possible inhalation and plant uptake for possible ingestion. While downward movement makes the plutonium less available for resuspension, its movement into the rooting zone for plants may increase plant uptake (Harley, 1980). Distribution of plutonium as well as of americium and radiocaesium in the soil profile is dependent at least on the following:

meteorological factors, type of soil, mixing of the soil layer, chemical form of the radionuclide, chemical composition of the soil, microbiological processes in the soil and the size of soil particles (Druteikiene and Luksiene, 1997). Somewhat greater downward migration of Am than of Pu has frequently been reported (Bunzl et al., 1992; Holm and Persson, 1978; Jia et al., 1999; Mboulou et al., 1998; Sokolik et al., 2001; Yamamoto et al., 1980).

Organic substances play an important role in the retention and relative mobility of Pu in the soil. A positive correlation between the organic matter content and Pu activity in soil has been reported by many authors (Kim et al., 1998; Komosa, 1999; Livens et al., 1987). The association of plutonium with organic molecules of different sizes has a direct effect on its mobility and biological availability in soil (Agapkina et al., 1995; Livens et al., 1987). Slow migration of Pu and Am in the organic layer probably is the result of complexation reactions with soil organic substances (Bunzl et al., 1995b). The concentration of Pu in soil has been reported to increase with clay content owing to the large surface area of clay per unit weight, which allows Pu to bind to the soil strongly through the many complexation sites (Kim et al., 1998).

A large portion of the Pu and Am in soil solutions is associated with colloidal and higher molecular weight fractions (Agapkina et al., 1995; Nisbet et al., 1993). Studies of Fujikawa et al. (1999) showed that at least 5 to 10% of Pu in the soil was strongly associated with humic acid and 1% with fulvic acid. Likewise, in the study of Livens and Singleton (1991), the activities were found to be four to five times as high in the humic acid fractions as in the fulvic acid fractions. The authors also presented evidence to suggest that americium was more concentrated than plutonium in the lower molecular weight fractions.

An important feature of plutonium in soil is resuspension, that is, its transfer along with resuspended particles of soil (Hanson, 1975). Different environmental conditions such as wind speed, temperature of the air, humidity, season of the year, geomorphological peculiarities of landscape, the amount of plant material, and the physico-chemical properties of soil influence the resuspension of plutonium (Druteikiene and Luksiene, 1997). Resuspension also depends on particle size (Hinton et al., 1995; Livens and Baxter, 1988).

Concentration of actinides into the fine particle size fraction of soil has been reported (Eakins et al., 1990; Yamamoto et al., 1980). Since the actinides are retained on the surface coating of soil, their distribution is a function of particle size. Yamamoto et al. (1980) report that the concentration of Pu increases with decreasing size of soil particles, while values for Am are more scattered. The authors suggest that the differences in particle size dependencies of the distributions of Pu and Am may have an effect on the resuspension and adsorption processes of these radionuclides.

The results of field observations and empirical laboratory test made by Mahara and Kudo (1988), indicate that mobile plutonium in soil is affected by the number of anaerobic bacteria. Micro-organisms can strongly influence the transport behaviour of actinides in soil by engaging in redox reactions, by regulating pore water chemistry, by degrading organic ligands that can complex radionuclides and by biosorption (Panak and Nitsche, 2001; Wang and Papenguth, 2001). Micro-organisms also produce organic acids capable of dissolving Pu (Francis, 2001).

Mietelski (2001) determined different vertical migration velocities of plutonium for the global fallout and Chernobyl fallout components in forest soil in Poland. The latter has about double the migration velocity of the former, according to Mietelski because of the difference in plutonium speciation or in particle size of Pu in the two components. Contrary to those results, Pavlotskaya et al. (1991) found no significant difference between the migration of fallout plutonium and Chernobyl-derived plutonium as in landscapes in Russia.

2.4.2 Radiocaesium in soil

The mobility of ^{137}Cs is strongly influenced by a number of properties of terrestrial ecosystems. Radiocaesium sorption by clays reduces its mobility (Shenber and Eriksson, 1993). ^{137}Cs is very efficiently captured by the clay structure because it does not have a tendency to hydrate when located in the clay interlayer space and it is therefore strongly bound to certain minerals, such as illite (Anderson, 1991). Sorption of ^{137}Cs is sensitive to the potassium and ammonium concentrations as well as to stable Cs in soil (Shenber and Eriksson, 1993). As a monovalent cation, ^{137}Cs is generally

assumed to exhibit cation-exchange characteristics and its release is assumed to be partly pH-dependent.

Many groups have reported ^{137}Cs association with organic material. In a study undertaken by Fawaris and Johansson (1994) in the coniferous forest ecosystem in Sweden, the thin humic layer strongly fixed radiocaesium, allowing only very slow migration of radiocaesium into the lower parts of soil profiles. Strandberg (1994) also observed a low penetration of ^{137}Cs in the soil, presumably due to binding to humus compounds since clay was almost absent. The author states that the relatively high bioavailability indicates that this binding is to some degree reversible. ^{137}Cs bioavailability is particularly high for organic soils since the presence of organic material reduces sorption of ^{137}Cs (Dumat et al., 1997). Usually, the interaction of ^{137}Cs with humic matter due to ion exchange with carboxylic or phenolic groups is rather unspecific (Bunzl et al., 1998a). Agapkina et al. (1995) report unexpected behaviour of ^{137}Cs in the organic soil horizon of a spruce forest, where ^{137}Cs was essentially associated with a single size fraction of the humic substances. The authors suggest that there must be a fairly strong association of ^{137}Cs with some specific organic compound. This unexpected behaviour of ^{137}Cs was also seen in a study conducted by Bunzl et al. (1998a) for grassland soil. According to these authors, the organic substance might have been derived from plant material in the initial stages of disintegration, or it might have been a product of the metabolism of micro-organisms.

The behaviour and stability of the microbial community of the forest floor are essential factors in the persistence, bioavailability, mobility and distribution of ^{137}Cs in forest soils (Rafferty et al., 1997). Autoclaved and nonautoclaved experiment on soils conducted by Sanchez et al. (2000) suggested microbial involvement in the process of radiocaesium sorption and retention by organic soils. Bunzl et al. (1995b) proposed that the long residence time of radiocaesium in the organic soil layer of pine forest was probably due to temporary immobilization and recycling processes originating in the presence of soil microflora, especially mycorrhizal fungi. Turnover of soil organic material is of dominant importance in ^{137}Cs transport in soils. After deposition at the soil surface, ^{137}Cs is mainly fixed by organic complexing and it is mobilised and refixed by microbial decomposition of organic material and dissolution of organic compounds (Tegen et al., 1991). Litter decomposition and ^{137}Cs release probably are influenced by

the nature and level of microbial activity in the soil and by the biochemical composition of the litter (Clint et al., 1990). Rafferty et al. (1997) also suggest that the role of Cs ion in plant physiology is important in determining its rate of mobilisation from decomposing litter.

2.5 Soil-to-plant transfer of radionuclides

The transfer of radionuclides to vegetation depends on 1) the type of vegetation, 2) the amount of contamination, 3) the biological accessibility of radionuclides determined by their physical and chemical characteristics in soil, 4) the soil characteristics and 5) the depth distribution of specific activity in soil (Poiarkov et al., 1995). As described by Baeza et al. (1999), once in the soil, each radioactive element follows complex dynamics in which a part of its concentration is transported into the soil solution, while another part gradually becomes strongly bound to the particles of the soil. The portion of the radionuclides that is present in the soil solution can be incorporated via the roots into plants. In some cases this is facilitated by the chemical similarity of the radionuclides with other elements that the plant normally uses for its growth.

2.5.1 Soil-to-plant transfer of Pu and Am

The importance of surficial contamination of vegetation by resuspended soil particles is widely recognized as a major pathway of actinides from soil to plant (Bunzl and Kracke, 1987; Copplestone et al., 1999; Copplestone et al., 2001; Hartmann and Bächmann, 1988; Nisbet and Shaw, 1994; Pimpl and Schüttelkopf, 1981). According to Watters et al. (1983), surficial contamination contributes 10 times more plutonium to vegetation than does transport across root membranes. Hartman and Bächmann (1988) reported that about 80% of the Pu in plant samples was present in the cuticula and on surfaces. Similarly, Pimp and Schüttelkopf (1981) reported that transfer factors were higher for plants whose surfaces were covered by hair, indicating that plutonium gets into plants by the surface contamination resulting from resuspension. Because of resuspension, transfer factors calculated from field observations are often larger than those from laboratory experiments (Bunzl and Kracke, 1987; Mudge et al., 1990; Pimpl and Schüttelkopf, 1981).

Greater uptake of americium than of plutonium by various plants been reported by Nisbet et al. (1993), Pimpl and Schüttelkopf (1981) and Price (1973). In contrast, Robinson et al. (2000) and Carini (2001) found no statistical differences between the transfer of Pu and Am from soil to fruits and vegetables. Mietelski et al. (2000) reported different behaviour of Pu and Am in lichens: the lichens retained plutonium more strongly than Am, which was partially leached out of thallia. Vyas and Mistry (1981) reported a marked reduction in uptake of both Pu and Am with increase in organic matter as well as clay content of soil. According to the authors, reduction in uptake with increasing clay content was more pronounced for Am than Pu.

2.5.2 Soil-to-plant transfer of radiocaesium

According to McGee et al. (2000) fungi, forest-floor vegetation and ruminant populations collectively contained about 1% of total radiocaesium fallout in a Swedish spruce forest. Vertical distribution of radiocaesium, percentage of exchangeable radiocaesium and distribution of root systems in the soil are key factors governing the radiocaesium availability for uptake by understorey components (Fesenko et al., 2001). Factors required to predict plant uptake of ^{137}Cs are soil clay content, exchangeable K status, pH, NH_4 concentration and organic matter content, as well as the effect of time on radiocaesium fixation (Absalom et al., 2001).

Potassium

Plant uptake of ^{137}Cs varies extensively between soils due differences in K availability, which affects the ^{137}Cs root uptake process (Smolders et al., 1997). ^{137}Cs displays very similar chemical properties to the biologically essential K^+ , and ^{137}Cs enters plants principally via the K transport system (Zhu and Smolders, 2000). Enhanced ^{137}Cs uptake is reported where the availability of potassium is low (Hinton et al., 1999; Varskog et al., 1994; Zach et al., 1989). Although ^{137}Cs and K are similar in mobility and uptake, no correlation of ^{137}Cs with K has been observed in mushrooms, indicating that the mechanism of ^{137}Cs uptake differs from that of K (Brunner et al., 1996; Yoshida and Muramatsu, 1998).

Acidity

Enhanced ^{137}Cs uptake at low pH has been reported by some authors (Hinton et al., 1999; Zach et al., 1989) while others have found hardly any effect of soil pH on the transfer factor of ^{137}Cs in the range pH 3.9 -8.4 (van Bergeijk et al., 1992).

Organic material

The organic matter content in soil appears to increase the uptake of ^{137}Cs by plants (van Bergeijk et al., 1992; Chiu et al., 1999), evidently due to the large cation exchange capacity of organic matter and the spatial distribution of organic substances around clay particles, which together prevent adsorption and subsequent fixation of ^{137}Cs on the clay minerals.

Rooting depth

Transfer of radiocaesium from soil to plants depends to a large extent on the concentration of this radionuclide in soil at the depth of the plant roots (Chiu et al., 1999; Pietrzak-Flis et al., 1996). Understorey plants take up radionuclides mainly from the organic horizons (Lux et al., 1995). In a study of Guillitte et al. (1994), the rooting depth of vascular plant was a key factor in the differences in contamination levels in stands of Scots pines, where deep-rooted species showed far less contamination than species with a superficial rooting system.

Time factor, climate

Studies on radionuclide soil-to-plant transfer have shown that the accumulation of ^{137}Cs has decreased with time, which reflects the changes in ^{137}Cs bioavailability (Krouglov et al., 1998). ^{137}Cs uptake rates at a given external ^{137}Cs concentration are higher in fast-growing species than in slower growing species. (Broadley et al., 1999). Transfer factors (see 4.4) are reported to be considerably lower in boreal forests than in temperate forests, and also lower in temperate regions than in subtropical or tropical regions (Carini, 2001; Guillitte et al., 1994). These differences are probably related to the duration of the growing season and the amount of rainfall (Guillitte et al., 1994).

Fungi, mycorrhizas, micro-organisms

Organisms occupying low trophic levels (fungi, micro-organisms, etc) appear to have ability to accumulate large amounts of ^{137}Cs (Avery, 1996; Brunner et al., 1996; Bürmann et al., 1994; Nikolova et al., 2000). Mushrooms are an important component in biological cycles in the forest environment, and transfer factors of ^{137}Cs for mushrooms are one to three orders of magnitude higher than those for plants (Tsukada et al., 1998). Symbiont mushrooms accumulate more caesium than saprophytic mushrooms (Guillitte et al., 1994; Kammerer et al., 1994). According to Guillitte et al. (1994), as much as 40% of the radiocaesium in soil may be eventually retained by the microflora, particularly by mycelia. It has been suggested that transport of ^{137}Cs from soil to plants is mediated by mycorrhiza fungi (Bürmann et al., 1994; Drissner et al., 1998).

3. SAMPLING SITES AND METHODS

3.1 Sampling sites

Research was performed in the vicinity of two Cu-Ni smelters: one in Monchegorsk, Russia (I, II, III), and the other in Harjavalta, Finland (IV, V) (see Fig. 1). The coordinates of the sampling sites as well as the distances from the smelters are given in Table 2.

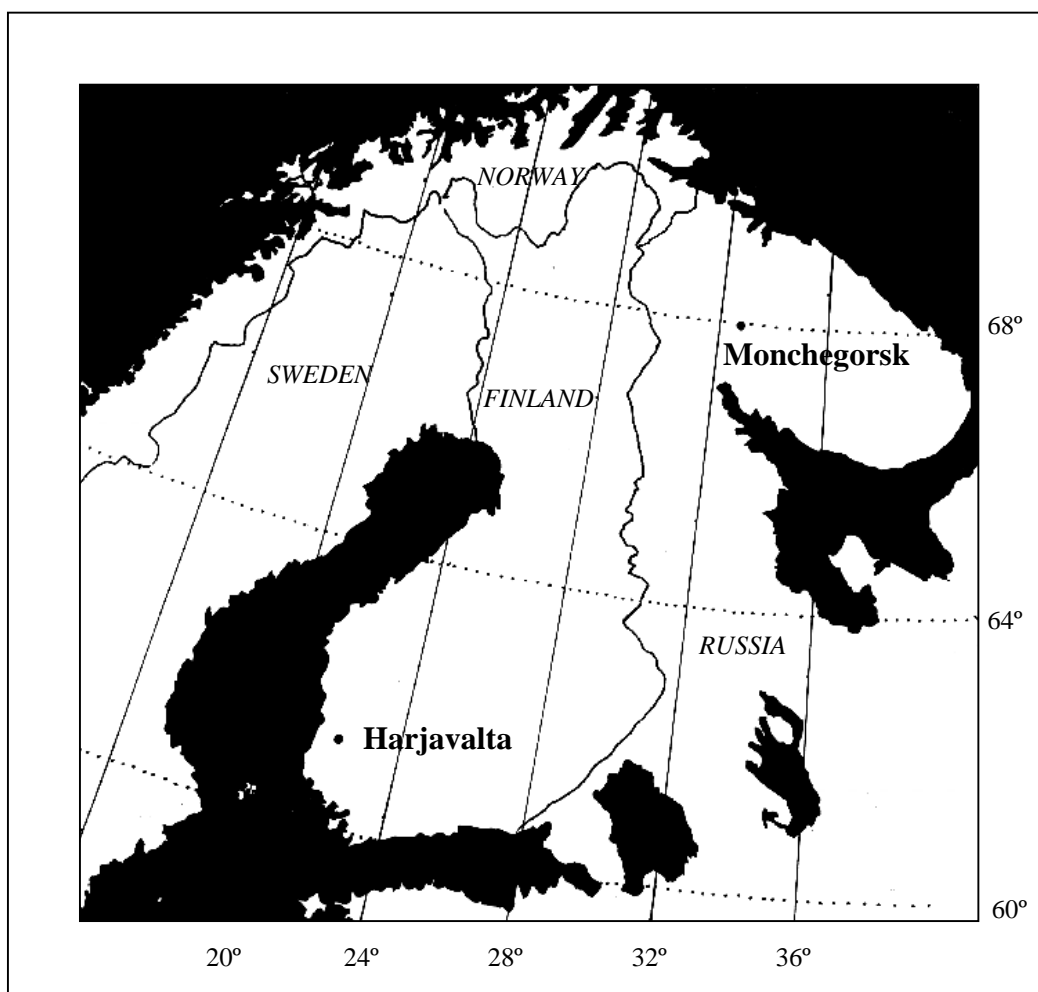


Figure 1. Location of Monchegorsk, Russia, and Harjavalta, Finland.

Table 2. Coordinates of the sampling sites in Monchegorsk and Harjavalta

Monchegorsk		Harjavalta	
Distance from the smelter (km)	Coordinates	Distance from the smelter (km)	Coordinates
7	67°51'N, 32°48'E	0.5	61°19'N, 22°07'E
14	67°46'N, 32°48'E	2	61°18'N, 22°08'E
21	67°44'N, 32°51'E	4	61°17'N, 22°08'E
27	67°40'N, 32°47'E	8	61°15'N, 22°12'E

The smelter in Monchegorsk commenced operations in 1938 and that in Harjavalta in 1945. During the period 1987-1991, annual emission levels in the Kola Peninsula as a whole were 500 000 tonnes of SO₂, 3700 tonnes of Ni and 2600 tonnes of Cu. In 1996, the corresponding amounts were 400 000, 1300 and 700 tonnes per year. Most of the Cu and Ni emissions come from the smelter in Monchegorsk. The annual emissions from Harjavalta are much lower than those from Monchegorsk and have decreased considerably during the 90's (see Fig. 2). In view of the differences in emission levels, the sampling sites in Harjavalta were selected closer to the smelter (0.5–8 km) than those in Monchegorsk (7 – 28 km).

The sampling sites in Monchegorsk were in spruce forest, while those in Harjavalta were in pine forest. As shown in in Table 3, the understorey vegetation in the two study areas differed to some extent. Sampling sites in Monchegorsk are described in detail by Rahola et al. (1999).

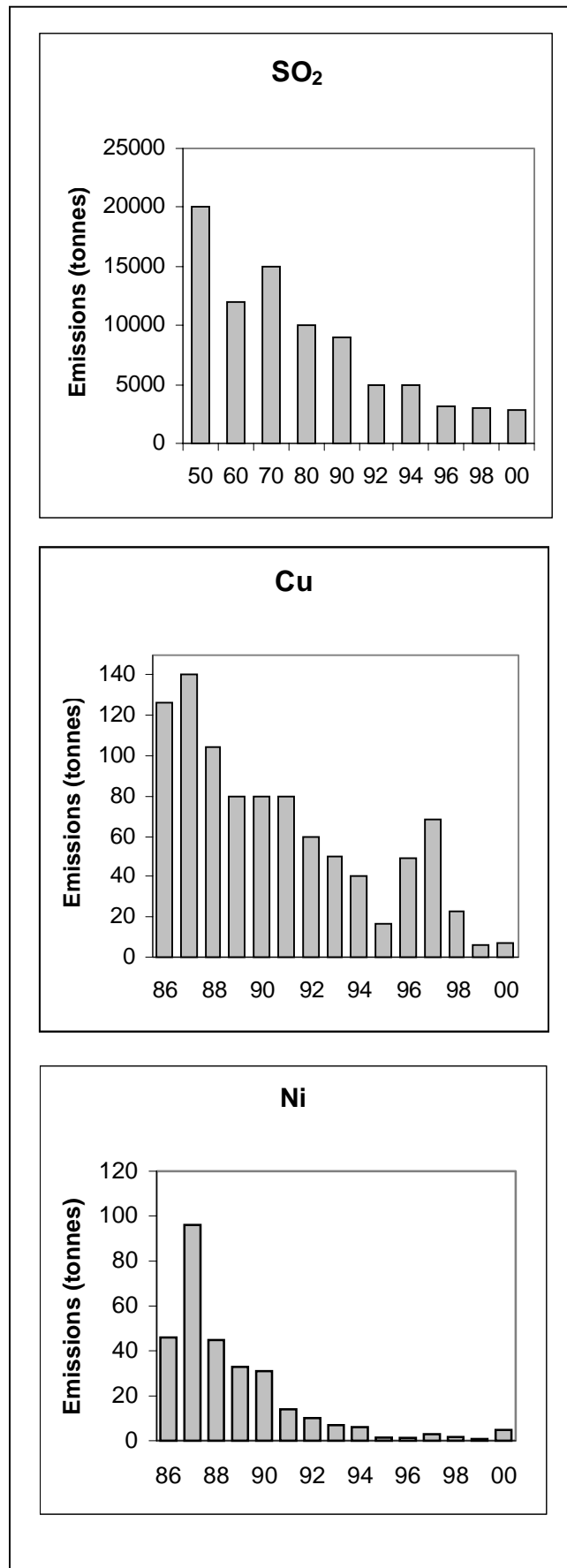


Figure 2. Annual emissions from the smelter in Harjavalta (Ruokonen, 2000)

Table 3. Understorey vegetation in Monchegorsk and Harjavalta.

Monchegorsk:	Harjavalta:
Spruce forest	Pine forest
<i>Empetrum nigrum</i>	<i>Empetrum nigrum</i>
<i>Vaccinium vitis-idaea</i>	<i>Vaccinium vitis-idaea</i>
<i>Vaccinium myrtillus</i>	<i>Cetraria islandica</i>
<i>Deschampsia flexuosa</i>	<i>Cladina stellaris</i>
	<i>Cladina rangiferina</i>
	<i>Cladina arbuscula</i>

Pollutants from Cu-Ni smelters have had diverse effects on the forest ecosystem. As shown in Table 4, at both Monchegorsk and Harjavalta there was a strong increasing gradient of accumulated heavy metals in the organic soil layer with decreasing distance to the smelter. In both areas concentrations of exchangeable K, Ca and Mg in the soil decreased with increased input of chemical pollutants (Thørring et al., 1999; Derome and Lindroos, 1998). No sign of soil acidification was found in the organic layer in Harjavalta, but there was an increase in exchangeable acidity and Al deeper in the mineral soil (Derome and Lindroos, 1998). Only minor variations were observed in soil pH and exchangeable acidity in Monchegorsk (Thørring et al., 1999). As reported by Derome & Nieminen (1998), at 0.5 km from the smelter in Harjavalta the water flux has been drastically altered as a result of damage to the tree stand and the ground vegetation. The water-holding capacity of the organic layer has been reduced and there is less chemical and microbiological interaction between the percolation water and soil. Fritze et al. (1989) report that total microbial mass and activity have decreased in the proximity of the smelter complex at Harjavalta owing to the toxic effect of Cu and Ni. The structure of the soil microbial community has changed as well (Pennanen et al., 1996). Likewise, the vegetation has been affected by industrial pollution: Salemaa et al. (2001) report that the total number of plant species in Harjavalta is 30 at 8 km from the smelter and only 8 at 0.5 km. Element concentrations in *Vaccinium vitis-idaea* collected from Monchegorsk and Harjavalta are shown in Table 5.

Table 4. Cu and Ni concentrations (mg/kg dry wt) in the organic soil layer at different distances from the smelters in Monchegorsk (Thørring et al., 1999) and Harjavalta (Derome and Lindroos, 1998).

Monchegorsk			Harjavalta		
Distance (km)	Cu	Ni	Distance (km)	Cu	Ni
7	1020	1630	0.5	5799	462
14	540	840	2	1648	224
21	380	680	4	658	124
27	310	490	8	147	39
152	8.6	8.1			

Table 5. Element concentrations (mg/kg dry wt) in *Vaccinium vitis-idaea* at different distances from the smelters in Monchegorsk (Thørring et al, 1999) and Harjavalta (IV).

Monchegorsk					Harjavalta				
Distance (km)	Cu	Ni	K	Ca	Distance (km)	Cu	Ni	K	Ca
7	390	340	2200	2900	0.5				
14	200	210	3400	5300	2	30	35	2500	6200
21	300	155	3800	4100	4	29	16	2900	6600
27	61	56	3600	3700	8	14	12	2500	7500
152	5.8	2.3	4400	5400					

3.2 Sampling

Litter and soil in Monchegorsk were sampled in August 1997. Samples were collected from five plots at each site. The size of the sampling plots was 1 m x 1.5 m, and the soil was sampled to a depth of 30 cm. In Harjavalta soil sampling was performed in September 2000 and soil profiles were taken with a corer having an inner diameter of

10.4 cm and length of 22 cm. Five soil profiles were taken at each site. At both Monchegorsk and Harjavalta the soil was separated into different horizons: litter (L), organic (O) and mineral (E and B) layers. Vegetation was collected at the sampling sites at the same time as soil by snipping with scissors. Mushrooms and lichens were collected by hand. Various mushroom species were found in Harjavalta, and all mushrooms were collected and combined for each site in order to have sufficient sample material. Vegetation was not washed before the activity determinations.

3.3 Analytical methods

The separation scheme for the determination of Pu and Am activities is shown in Fig. 3. The procedure is also discussed in paper V. Pu was separated by anion exchange (Dowex 1x4, 50–100 mesh), which was performed twice. Am was purified with use of extraction chromatography resins TRU and TEVA, obtained from Eichrom's Industries. Mean Pu recoveries varied between 80 and 100% for the different sample matrices, and those of Am between 70 and 90%. Extraction chromatography was also tested for plutonium, but recoveries of Pu obtained with extraction chromatography resins (UTEVA and TRU) were lower than those obtained by anion exchange, so anion exchange was preferred. Alpha activities were measured with surface barrier detectors or passivated implanted planar silicon (PIPS) detectors for 1 to 10 days. Gamma activities were measured with a high purity Ge-detector.

Chemical forms of radionuclides were determined by using the sequential extraction method developed by Tessier et al. (1979) and modified by Bunzl et al. (1995). The soil was extracted into four fractions: exchangeable (I), bound to oxides (II), bound to organic material (III) and persistently bound (IV). Reagents were

I	1 M $\text{CH}_3\text{COONH}_4$
II	0.04 M NH_2OHHCl in 25 vol% HAc at pH 2
III	30% H_2O_2 at pH 2
IV	7 M HNO_3

^{137}Cs was also determined in the residual fraction (V). The soil to reagent ratio was 1:10. The procedure is described in more detail in paper I.

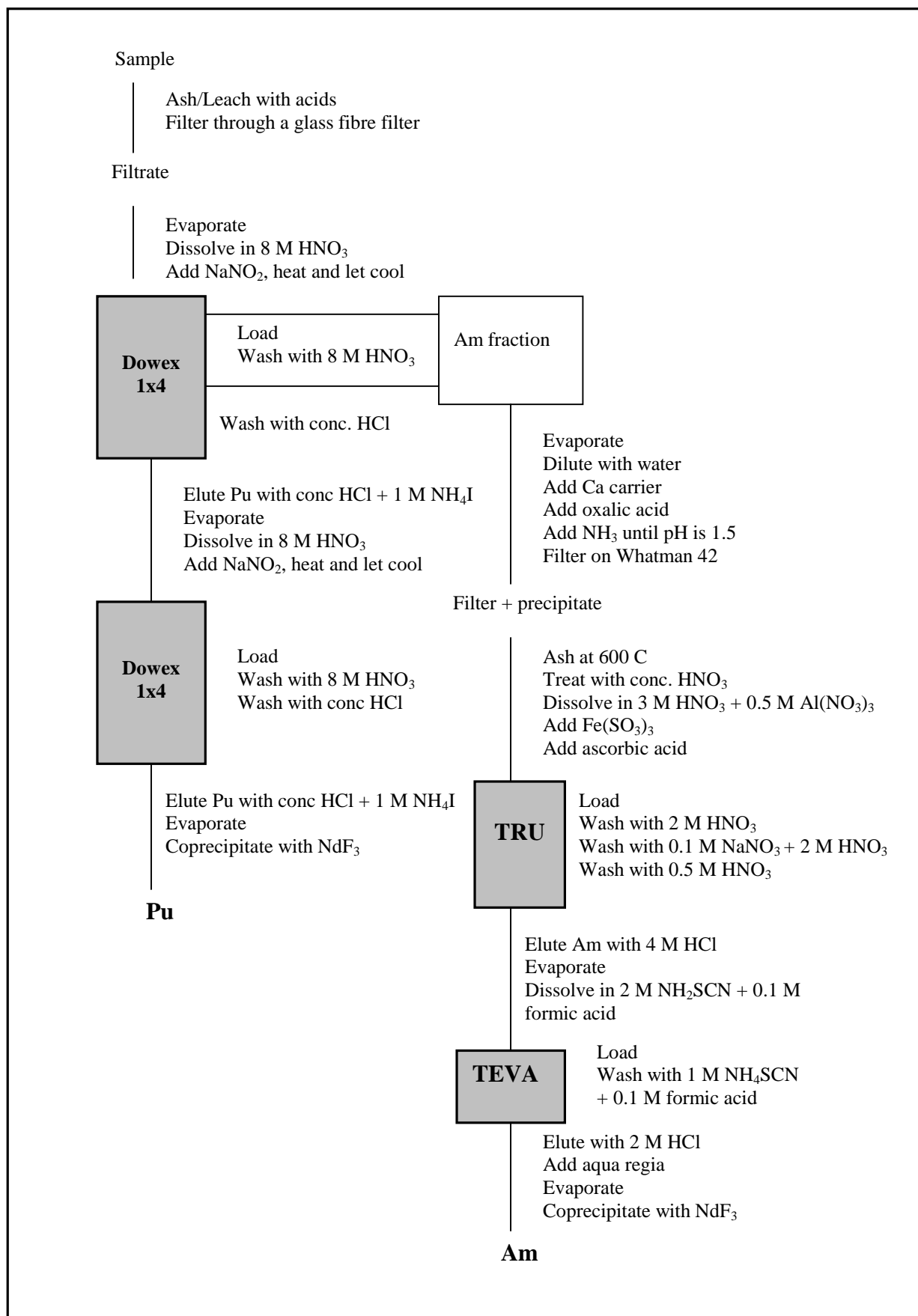


Figure 3. Separation scheme for Pu and Am from environmental samples.

4. RESULTS AND DISCUSSION

4.1 Radionuclides in forest soils contaminated by industrial pollution

Designations used for soil horizons in this study are L, O, E and B. The litter layer, L (also called O_i in the literature,) consists mainly of undecomposed organic material such as needles and leaves. The litter contains abundant nutrients, which are recycled in the soil through decomposition. The organic horizon, O, is dominated by organic material decomposed to various levels. The mineral layer E is characterised by an eluvial loss of silicate clay, iron and aluminium. Usually the E horizon is lighter in colour than the underlying B horizon. The mineral layer B is characterised by illuvial accumulation of silicate clay, iron and aluminium.

4.1.1 Distributions of $^{239,240}\text{Pu}$ and ^{241}Am in soil (II, III, V)

Distribution of $^{239,240}\text{Pu}$ among the various soil horizons along the pollution gradients in Monchegorsk and Harjavalta is shown in Fig. 4. Most of the plutonium in the soils was present in the organic layer and the litter layer. In both areas the amount of $^{239,240}\text{Pu}$ in litter increases towards the smelters, whereas the amount of plutonium present in the organic layers decreases. The reason for the increasing content of $^{239,240}\text{Pu}$ in litter and the decreasing content of $^{239,240}\text{Pu}$ in the organic layer as a function of pollution is the low level of microbial activity near the smelter. In their study of the soil microbial effects of the Cu-Ni smelter in Harjavalta Fritze et al. (1989) found that both the numbers of bacteria and soil respiration decreased towards the smelter. The low microbial activity caused by high Cu and Ni concentrations and acid deposition suppress the decomposition of litter, increasing the volume of the litter and decreasing the thickness of the organic layer. The thick layer of litter at the most polluted sites retains plutonium, preventing it from migrating downwards to deeper layers and causing a high $^{239,240}\text{Pu}$ concentration in the litter itself.

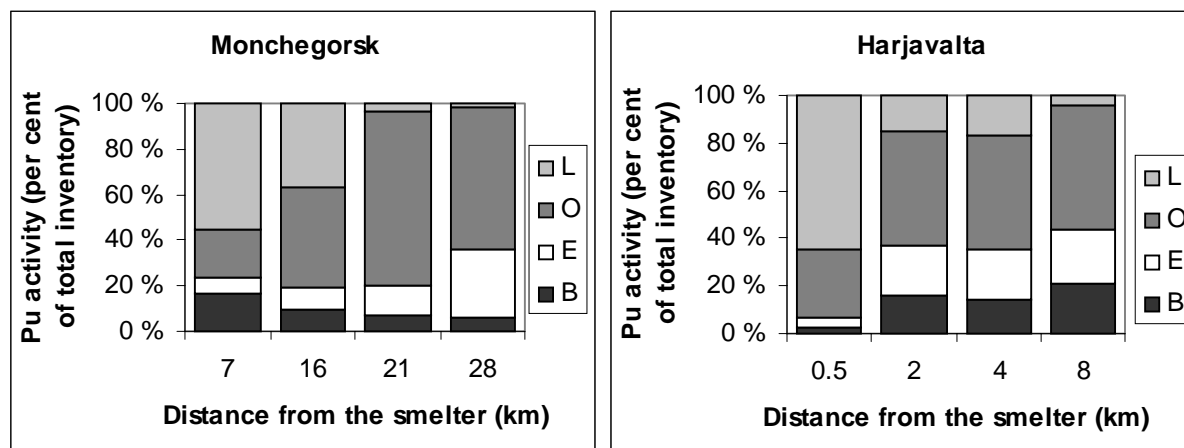


Figure 4. Distribution of $^{239,240}\text{Pu}$ among litter (L), organic (O) and mineral layers (E and B) along the pollution gradient in Monchegorsk and in Harjavalta.

Figure 5 shows the distribution of ^{241}Am in soil along the pollution gradient in Harjavalta. The effect of industrial pollution on the distribution of ^{241}Am was similar to that of $^{239,240}\text{Pu}$. More Am was bound to litter and less to the organic soil layer towards the smelter. $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio in soil before the Chernobyl accident is reported to have been about 0.3 (Yamamoto et al., 1985). ^{241}Am is mostly formed in situ through decay of ^{241}Pu . Mboulou et al. (1998) report an $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio of 0.8 for topsoil close to Chernobyl. In the litter layer the $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio decreased towards the smelter from 0.8 ± 0.1 at 8 km to 0.41 ± 0.03 at 0.5 km. This is due to larger amounts of global fallout radionuclides retained in the litter layer towards the smelter where litter decomposition is inhibited. The average $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio was 0.43 ± 0.04 for organic horizons and 0.3 ± 0.1 for the mineral horizons (V). Higher $^{241}\text{Am}/^{239,240}\text{Pu}$ ratios detected in topsoil are due to Chernobyl deposition, which contains higher $^{241}\text{Pu}/^{239,240}\text{Pu}$ ratio than the deposition from global fallout. $^{239,240}\text{Pu}$ and ^{241}Am from Chernobyl are mainly retained in litter, some migrating into the organic layer, but no Chernobyl-derived $^{239,240}\text{Pu}$ and ^{241}Am were detected in the mineral soil.

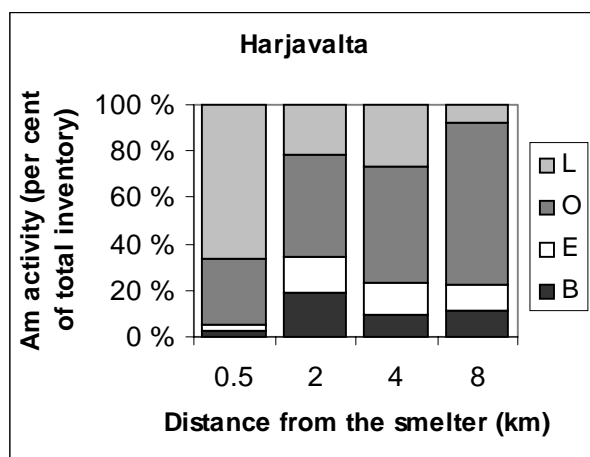


Figure 5. Distribution of ^{241}Am among litter (L), organic (O) and mineral layers (E and B) along the pollution gradient in Harjavalta.

4.1.2 Distribution of ^{137}Cs in soil (II, IV)

The distribution of ^{137}Cs among the different soil horizons in Monchegorsk and Harjavalta is shown in Fig. 6. The different distributions of ^{137}Cs in the two areas are due to the different origin of ^{137}Cs . In Harjavalta approximately 90% of the ^{137}Cs activity is from Chernobyl (IV), while in Monchegorsk only 10% of it is Chernobyl-derived, and most is from global fallout (II). Because ^{137}Cs has not had sufficient time to penetrate into the mineral layers in Harjavalta in the same degree as it has done in Monchegorsk, the litter layer contains a higher percentage of ^{137}Cs . In both areas, more ^{137}Cs was bound to litter and less to the organic horizon in the direction of the smelter.

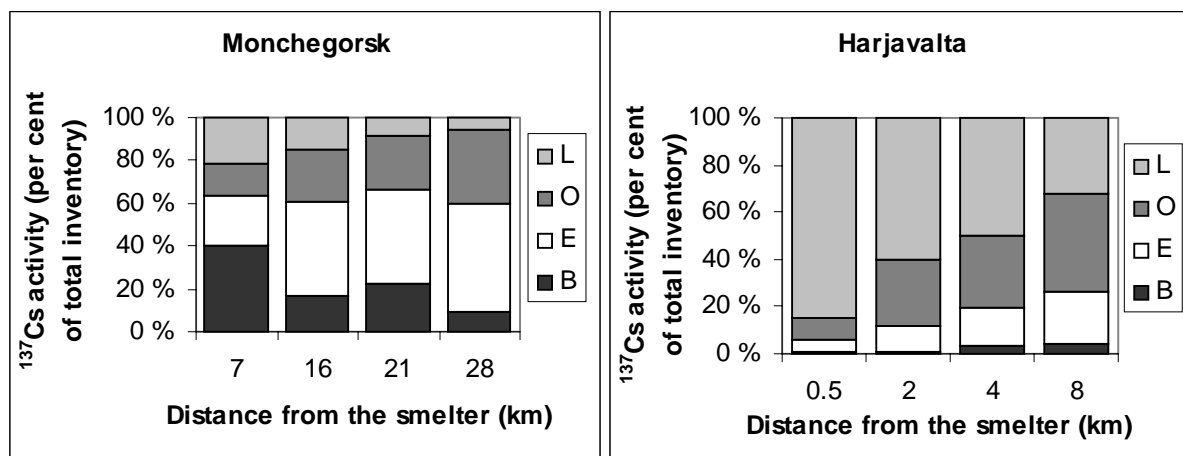


Figure 6. Distribution of ^{137}Cs among litter (L), organic (O) and mineral layers (E and B) along the pollution gradient in Monchegorsk and Harjavalta.

4.1.3 Total depositions of radionuclides in soil (II, III, IV, V)

Total depositions of radionuclides were measured in the upper 20 cm of soil. In Monchegorsk, total deposition of $^{239,240}\text{Pu}$ decreases from 47 Bq/m^2 to 28 Bq/m^2 towards the smelter (III). It was suggested (III) that erosion and migration of $^{239,240}\text{Pu}$ deeper into the mineral soil was the reason for this behaviour. In Harjavalta, in turn, no effect of industrial pollution was detected on total deposition of $^{239,240}\text{Pu}$ or ^{241}Am in soil, values ranging between 42 and 51 Bq/m^2 for $^{239,240}\text{Pu}$ and from 17 to 23 Bq/m^2 for ^{241}Am (V). The amount of Chernobyl-derived plutonium in soil in Harjavalta was 0.5 – 1.8 Bq/m^2 (V), whereas no Chernobyl-derived plutonium was detected in Monchegorsk (III). The $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio in soil cores in Harjavalta varies between 0.40 and 0.45 (V). Industrial pollution had no effect on the total deposition of ^{137}Cs . Total deposition of ^{137}Cs varied between 15 and 25 kBq/m^2 (Sept., 2000) in Harjavalta (IV) and between 1.2 and 1.8 kBq/m^2 (August, 1997) in Monchegorsk (II). Our measured total deposition values are in good agreement with literature values of $^{239,240}\text{Pu}$ and ^{137}Cs (Hardy et al., 1973; Arvela et al., 1990; Saxen et al., 1987)

4.2 Effect of industrial pollution on chemical forms of radionuclides in forest soil

Effect of industrial pollution on the chemical forms of radionuclides was studied in detail in Monchegorsk and the results are discussed in paper III. Chemical forms of radionuclides in Harjavalta were studied only at a distance of 8 km from the smelter, in order to determine if there were any major differences between Harjavalta and Monchegorsk. The soil was extracted into four fractions: exchangeable (I), bound to oxides (II), bound to organic material (III), and persistently bound (IV).

4.2.1 Chemical forms of $^{239,240}\text{Pu}$ and ^{241}Am (I)

At every site in Monchegorsk 85-90% of the plutonium was bound to organic material. 1-6% of Pu was exchangeable, less than 1% was bound to oxides and approximately 10% was persistently bound. The only effect of pollution on the chemical forms of plutonium was detected in the exchangeable fraction: there was less exchangeable plutonium (1%) at the site closest to the smelter than at the sites further away (4-6%). The difference is due to the higher content of mineral material in the organic layer at the site closest to the smelter.

Figure 7 shows the associations of plutonium with various soil fractions at the most distant sites from the smelters in Monchegorsk (28 km) and Harjavalta (8 km), and the association of americium at the same site in Harjavalta. In Harjavalta, just as in Monchegorsk, most of the plutonium is bound to organic material (93%). The main difference is that there is less exchangeable plutonium (1.6%) in Harjavalta than in Monchegorsk (6.3%). Americium was associated with soil constituents similarly to plutonium. Contrary to our findings, Bunzl et al. (1985) and Ibrahim and Salazar (2000) have reported that, relative to plutonium, more americium in soil was present in exchangeable form.

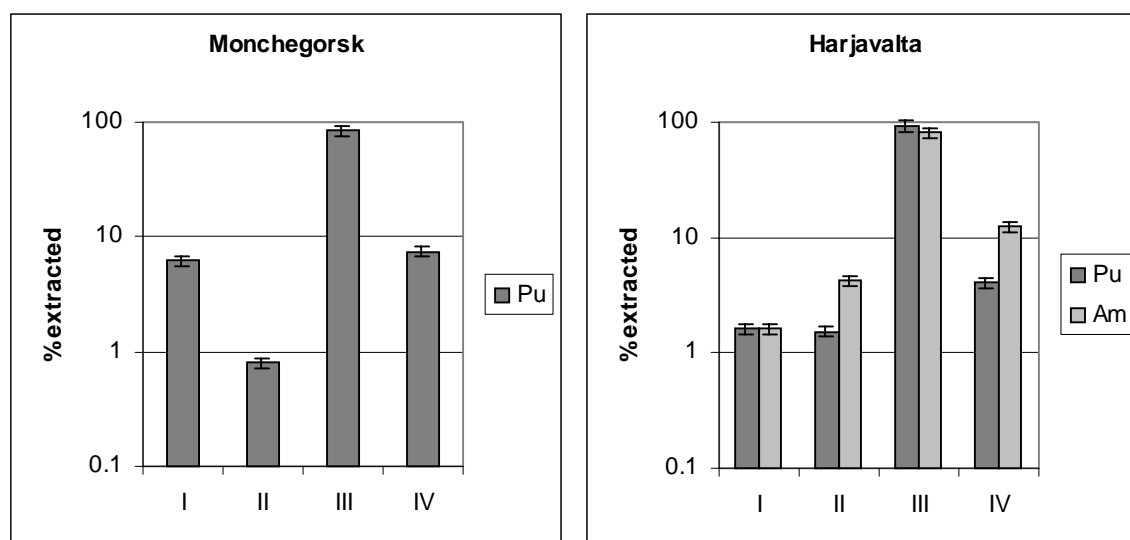


Figure 7. Association of $^{239,240}\text{Pu}$ and ^{241}Am with various soil fractions as determined by sequential extraction: I exchangeable, II bound to oxides, III bound to organic matter and IV Persistently bound. Results from Monchegorsk are for a distance of 28 km from the smelter and those from Harjavalta for a distance of 8 km from the smelter. The uncertainties are given as one standard deviation.

4.2.2 Chemical forms of ^{137}Cs (I)

In Monchegorsk most ^{137}Cs was found in the persistently bound fraction, the exchangeable fraction and the residual fraction. The amount of ^{137}Cs in the exchangeable fraction decreased with increase in the pollution load. Mineral content of the organic layer was higher at the site closest to the smelter and may lead to stronger fixation of ^{137}Cs (I). Figure 8 shows the association of ^{137}Cs with different soil fractions at the sites furthest from the smelter in Monchegorsk (28 km) and in Harjavalta (8 km). Less ^{137}Cs exists in exchangeable form (similarly to the results for plutonium) and more in the residual fraction in Harjavalta than in Monchegorsk.

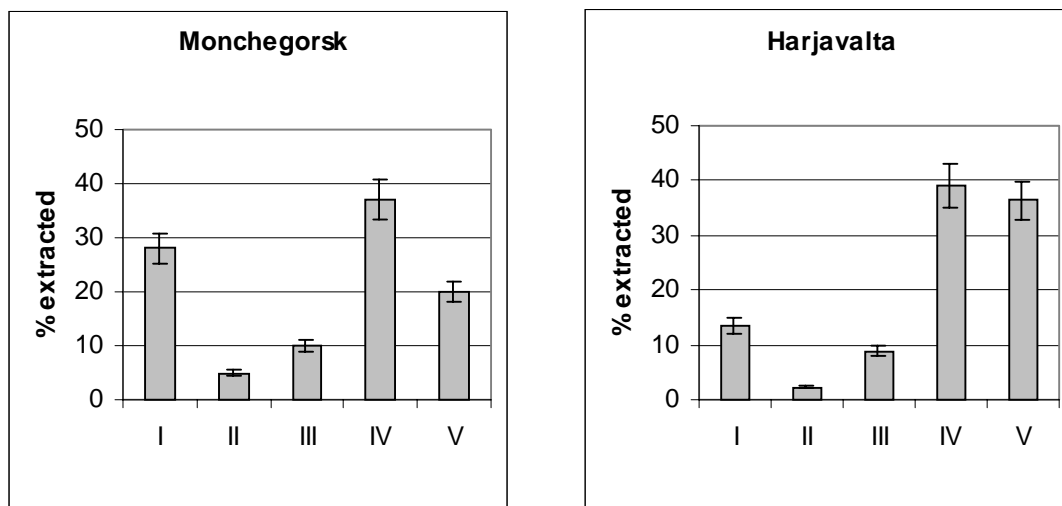


Figure 8. Association of ^{137}Cs with various soil fractions as determined by sequential extraction: I exchangeable, II bound to oxides, III bound to organic matter, IV persistently bound and V residual. Results from Monchegorsk (mean values of five analyses) are for a distance of 28 km from the smelter and those from Harjavalta for a distance of 8 km from the smelter. The uncertainties are given as one standard deviation.

4.3 Effect of industrial pollution on radionuclides in vegetation

In the absence of direct deposition from air the concentration of radionuclides in plants is due to root uptake and surface contamination with resuspended litter. Concentration in plants depends on the concentration in soil. In the case of plutonium, total deposition in soil was similar in Monchegorsk and Harjavalta, but in the case of ^{137}Cs the total deposition was much higher in Harjavalta due to the Chernobyl deposition. Comparisons are thus made not of concentration in plants but of transfer factors, as discussed in section 4.4. The effect of pollution on the transfer of radionuclides from soil to plants, as well as the differences between Monchegorsk and Harjavalta, will be discussed in section 4.4..

4.3.1 $^{239,240}\text{Pu}$ and ^{241}Am in vegetation (III, V)

Pu concentrations in dwarf shrubs varied between 1 and 19 mBq/kg in Monchegorsk (III); the concentrations were lower in Harjavalta, varying from 0.4 to 2.6 mBq/kg (IV). In Harjavalta, concentrations in lichens varied from 3.8 to 10 mBq/kg and concentrations in mushrooms from 5.5 to 20 mBq/kg (V). Am concentration in vegetation of Harjavalta was quite similar to that of plutonium, varying from 0.5 to 2.5 mBq/kg for dwarf shrubs, from 3.5 to 12.3 mBq/kg for lichens and from 5.5 to 10.4 mBq/kg for mushrooms (V).

$^{241}\text{Am}/^{239,240}\text{Pu}$ ratios in vegetation at Harjavalta varied between 0.4 ± 0.1 and 1.8 ± 0.7 (V). Though the uncertainties are relatively high, $^{241}\text{Am}/^{239,240}\text{Pu}$ ratios seem to decrease in vascular plants and mushrooms towards the smelter. No trend was seen in $^{241}\text{Am}/^{239,240}\text{Pu}$ ratios in lichens (V). Lower $^{241}\text{Am}/^{239,240}\text{Pu}$ ratios in plants close to the smelter suggest that 1) plants take up these radionuclides from deeper in the soil where lower $^{241}\text{Am}/^{239,240}\text{Pu}$ ratios were detected or 2) plants are contaminated with resuspended litter, which has lower $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio towards the smelter.

4.3.2 ^{137}Cs in vegetation (IV)

Concentration of ^{137}Cs in plants differed greatly in these two areas due to the different levels of deposition: about 2 kBq/m² in Monchegorsk and 25 kBq/m² in Harjavalta. Because of the different deposition, concentration in plants are not meaningfully compared and it is more useful to compare transfer factors (see section 4.4) where deposition is included in the formula. In Harjavalta, the concentration of ^{137}Cs in dwarf shrubs, mushrooms and lichens decreased towards the smelter. Concentration range was 20-1500 Bq/kg for dwarf shrubs, 1000-40000 Bq/kg for mushrooms and 170-1500 Bq/kg for lichens (IV). In Monchegorsk, ^{137}Cs concentration decreased with increasing pollution load for *Vaccinium myrtillus* and *Empetrum nigrum*, but it increased for *Deschampsia flexuosa* (Bunzl et al., 1999). According to Bunzl et al. (1999), concentration in plants in Monchegorsk varied from 10 to 70 Bq/kg.

4.4 Effect of industrial pollution on soil-to-plant transfer of radionuclides

Transfer of radionuclides from soil to plants is usefully described with the aggregated transfer factor or the concentration ratio. The concentration ratio is designed especially for agricultural soil and is defined as concentration in plants (Bq/kg) divided by concentration in soil (Bq/kg) within the uppermost soil layers. The basic assumption is that the radionuclide concentration is homogeneous in soil, which is not the case in forest soil with its pronounced vertical profile of activity concentration. The aggregated transfer factor (T_{ag}), which is defined as the activity in plants (Bq/kg) divided by the total deposition in soil (Bq/m²), is more suitable for forest environment. The main disadvantage of T_{ag} is that it does not take account of the rooting depth of plants or soil horizons from which nutrients are taken. Although it is possible to calculate transfer factors for specific soil horizons, this requires knowledge of the rooting depths of the plants of interest. Aggregated transfer factors were used in this study because the rooting depth of the plants was not evident at all sites, as will be discussed below, and this concept also takes account of surficial contamination, in addition to the root uptake of radionuclides.

Different understorey vegetation was growing in Monchegorsk (spruce forest) and Harjavalta (pine forest) as shown in table 3. However, *Empetrum nigrum* and *Vaccinium vitis-idaea* were growing in both sampling areas and the findings for these two plants at Monchegorsk and Harjavalta will be compared in some detail.

4.4.1 Soil-to-plant transfer of ^{239,240}Pu and ²⁴¹Am (III, V)

Root uptake of Pu and Am from soil to plants is extremely low. Surficial contamination of plants by resuspended soil particles is more important for both Pu and Am. Table 6 presents the transfer factors of plutonium for *Vaccinium vitis-idaea* and *Empetrum nigrum* along pollution gradients in Monchegorsk and Harjavalta. Transfer factors are smaller in Harjavalta than in Monchegorsk. Sequential extraction studies (Fig. 7) showed that plutonium is less easily available (plant available) in Harjavalta than in

Monchegorsk and this may partly explain the differences in transfer factors between the two locations.

Table 6. Transfer factors (T_{ag}) of plutonium for *Vaccinium vitis-idaea* and *Empetrum nigrum* at different distances from the smelters at Monchegorsk (III) and at Harjavalta (V). The uncertainties are given as one standard deviation.

Monchegorsk		Harjavalta	
Distance (km)	T_{ag} (10^{-5} m ² /kg)	Distance (km)	T_{ag} (10^{-5} m ² /kg)
<i>Vaccinium vitis-idaea</i>			
7	8.1±1.7	0.5	-
14	20±3	2	0.8±0.3
21	6.1±1.0	4	1.6±0.3
27	13±2	8	1.7±0.5
<i>Empetrum nigrum</i>			
7	51±4	0.5	-
14	60±6	2	5.1±0.7
21	26±3	4	3.7±0.5
27	7.3 ±1.0	8	3.2±0.7

In Monchegorsk an increasing amount of Pu is transferred from soil to *Empetrum nigrum* towards the smelter. A similar effect was observed for *Vaccinium myrtillus* and *Deschamsia flexuosa* (III). This is due to contamination by resuspended soil particles. Pu content of litter increased with pollution load as shown in Fig. 4. Similar behaviour was not detected for *Vaccinium vitis-idaea* and it was speculated (III) that resuspension is not as important factor for *Vaccinium vitis-idaea* as it is for the other plants, possibly because of the structure of the leaves. The leaves of *Vaccinium vitis-idaea* have a shiny upper surface, and perhaps the soil particles do not adhere to the surface of the leaves as tightly as to those of the other plants.

In Harjavalta, T_{ag} of Pu increased for mushrooms (from 1.2×10^{-5} to 4.9×10^{-5} m²/kg) towards the smelter, but no significant trend was seen for *Empetrum nigrum* nor

Vaccinium vitis-idaea. Possibly root uptake of Pu decreases more in Harjavalta than in Monchegorsk as the load of industrial pollution increases. This could explain why the transfer factors do not increase with pollution load in Harjavalta as they did in Monchegorsk. Another explanation could be that resuspension is less important in pine forest (Harjavalta) than in spruce forest (Monchegorsk), owing to differences in the composition of the litter.

Transfer factors of Am were usually higher than those of Pu (V). Higher uptake of Am than Pu by vegetation is also reported by Price (1973), Nisbet et al. (1993), Pimpl and Schüttelkopf (1981). The effect of pollution on T_{ag} of Am was different from the effect on T_{ag} of Pu. For *Vaccinium vitis-idaea*, the transfer factor of Am decreased more than that of Pu with increasing pollution. For mushrooms, no trend was detected though T_{ag} of Pu showed a clear positive trend with pollution (V). This suggests that either uptake of Am by vegetation decreases more strongly than that of Pu or that Am does not contaminate the vegetation in resuspended particles similarly to Pu. Yamamoto et al. (1980) observed differences in particle size dependencies of the distributions of Pu and Am and, in their view, this may have an effect on the resuspension and adsorption processes of these radionuclides.

4.4.2 Soil-to-plant transfer of ^{137}Cs (V)

Transfer factors of ^{137}Cs for dwarf shrubs at Monchegorsk and Harjavalta are presented in Table 7. At the two sites most distant from the smelters, transfer factors were similar for *Empetrum nigrum*, but evidently higher for *Vaccinium vitis-idaea* at Harjavalta. One explanation of this difference is that the roots of *Vaccinium vitis-idaea* are more superficial than those of *Empetrum nigrum* and the concentrations of ^{137}Cs in topsoil were higher in Harjavalta due to Chernobyl deposition.

In Harjavalta, T_{ag} of ^{137}Cs for all plants decreased significantly as the industrial pollution load increased (IV). One reason for the decreasing transfer factors with pollution is the lower content of ^{137}Cs in the organic layer at sites close to the smelter (Fig 5). Another reason is that in the vicinity of the smelter in Harjavalta roots of the plants penetrate deeper into mineral soil, as reported by Uhlig et al. (2001). Mineral soil contains much less ^{137}Cs than the organic layer, where plant roots normally are found.

In Monchegorsk, T_{ag} for *Empetrum nigrum* decreased with increasing pollution, but the decrease was weaker than in Harjavalta. No clear change with pollution was seen in the transfer factor for *Vaccinium vitis-idaea* (Bunzl et al., 1999). Why did the transfer factors of ^{137}Cs not decrease as significantly in Monchegorsk as they did in Harjavalta? Possibly the roots did not penetrate into the mineral soil layer to the extent they did in Harjavalta because the organic layer was thicker in Monchegorsk than in Harjavalta. The mineral soil layer in Monchegorsk also exhibited a higher percentage of ^{137}Cs activity than the mineral soil layer in Harjavalta (Fig. 6).

Table 7. Transfer factors (T_{ag}) of ^{137}Cs for *Vaccinium vitis-idaea* and *Empetrum nigrum* at different distances from the smelter at Monchegorsk (Bunzl et al., 1999) and at Harjavalta (IV). The uncertainties are given as one standard deviation.

Monchegorsk		Harjavalta	
Distance (km)	$T_{ag} (10^{-3} \text{ m}^2/\text{kg})$	Distance (km)	$T_{ag} (10^{-3} \text{ m}^2/\text{kg})$
<i>Vaccinium vitis-idaea</i>			
7	12	0.5	-
14	14	2	0.7 ± 0.3
21	13	4	37 ± 10
27	18	8	76 ± 12
<i>Empetrum nigrum</i>			
7	7	0.5	-
14	11	2	0.8 ± 0.3
21	10	4	9.2 ± 2.5
27	15	8	16 ± 3

5. CONCLUSIONS

The effect of industrial pollution on the behaviour of radionuclides was studied in the vicinity of two Cu-Ni smelters: one in Monchegorsk, Russia, and the other in Harjavalta, Finland. The main differences between these two areas were the composition of the radioactive deposition and the type of forest. In Harjavalta, the major part of the ^{137}Cs deposition and a significant part of the Pu and Am deposition were due to the accident at Chernobyl, while in Monchegorsk the radionuclides were almost entirely derived from global fallout. Sampling sites in Harjavalta were in pine forest, whereas those in Monchegorsk were in spruce forest.

Industrial pollution had a significant effect on the distribution of radionuclides in soil horizons. With the increase in pollution towards the smelter, radionuclides were accumulated more in the litter layer because the conversion of litter into organic material was diminished due to inhibited microbial activity. As a result, the organic layer contained less radionuclides towards the smelter.

The studies on the effect of industrial pollution on chemical forms of radionuclides indicated that the amounts of easily available plutonium and radiocaesium decreased slightly with increasing load of industrial pollution. The sequential extraction study performed in Harjavalta showed similar behaviour of americium and plutonium in organic soil. Only a small portion of the amount of these radionuclides in soil is available for plants. Less plutonium and radiocaesium were easily available in the organic layer of soil in the pine forest at Harjavalta than in the spruce forest at Monchegorsk.

The effect of industrial pollution on soil-to-plant transfer was complex. The effect varied with radionuclide, plant species and also on forest type and origin of deposition. For ^{137}Cs , soil-to-plant transfer decreased significantly as industrial pollution increased in pine forest contaminated mainly with Chernobyl-derived radiocaesium, whereas the decrease was less pronounced for global fallout radiocaesium in spruce forest. It is suggested that the huge decrease in the transfer factor of ^{137}Cs close to the smelter in pine forest is caused by the penetration of roots of the plants deeper into mineral layers.

^{137}Cs concentration is significantly lower in mineral soil than in the organic layer where roots of the plant normally are found.

Root uptake of Pu and Am by plants is extremely small, and plant contamination by resuspended soil is the important factor in considering the soil-to-plant transfer of these radionuclides. In spruce forest, soil-to-plant transfer of Pu increased with industrial pollution due to resuspension of litter, which contained higher concentrations of Pu in the vicinity of the smelter. Soil-to-plant transfer of Pu was much less affected in pine forests. More Am than Pu was transferred from soil to plants in pine forest.

This research clearly indicates the sensitivity of the northern forest ecosystem to inorganic pollutants. Prediction of the soil-to-plant transfer of radionuclides in industrially polluted forest ecosystems requires detailed information on the total deposition and vertical distribution of radionuclides in soil, on soil microbiological factors and other soil parameters, as well as on the rooting depths of plants.

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